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(54) Title: METHOD FOR MAKING CATALYSTS CONTAINING SILICOALUMINOPHOSPHATE MOLECULAR SIEVE AND CATALYST THUS PREPARED (57) Abstract A method for making a catalyst comprising forming a mixture comprising an inorganic sol and a silicoaluminophosphate molecular sieve having pores of a diameter less than about 5 Angstroms, and drying the mixture. The present invention is also directed to a catalyst including a silicoaluminophosphate molecular sieve having pores of a diameter less than 5 Angstroms; and an aluminum oxide matrix derived from an alumina sol.		

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Method for making catalysts containing silicoaluminophosphate molecular sieve and catalyst thus prepared

Field of the Invention

The present invention relates to catalysts comprising small pore silicoaluminophosphate molecular sieves for hydrocarbon conversions and oxygenate conversions, and a method for making the catalysts.

Background of the Invention

Many hydrocarbon conversions and oxygenate conversions are used in the petrochemical, chemical and refining industries. The conversion processes produce olefins, gasoline, fuel oils, and many other valuable products. Most of the processes are catalyzed by molecular-sieve containing catalysts. Hydrocarbon cracking -- a widely practiced hydrocarbon conversion -- is an endothermic conversion which commonly is practiced in a fluid catalytic cracking (FCC) mode or in a moving bed cracking mode. Heat must be provided for an endothermic conversion. Oxygenate conversion is an exothermic conversion. Different operating modes, including fixed bed, fluidized bed and moving bed modes, also have been used and tested for oxygenate conversions. Heat must be removed for an exothermic conversion.

Both fluidized bed and moving bed processes commonly are carried out in a cyclic mode. The hydrocarbon and oxygenate feedstocks are contacted in a reactor with hot, active catalysts particles at an elevated temperature and a modest pressure. As the feedstocks are converted to the desired valuable products, undesirable residue known as coke forms on the catalyst. The coke tends to cause the catalyst to lose its activity and become deactivated. The deactivated particulate catalysts then are disengaged from the feedstock, sometimes stripped of residual hydrocarbons, and sent to a regenerator for regeneration. Regeneration usually is carried out at elevated temperature with a controlled burn of the coke in the presence of oxygen and a diluent inert gas to minimize unintended temperature surges. In some cases, regeneration is effected by hydrogen stripping at elevated temperature.

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The catalysts used in these conversions usually are fine powders with a particle size in the range of from about 20 to 250 microns in diameter, most typically averaging in the range of from about 50 to about 150 microns in diameter. If the catalyst particles are too large in diameter, then the particles will not possess the
5 needed fluidization and other flow properties for fluidized-bed and moving-bed processes. If the particles are too small in diameter, then the particles will be carried out of the reactor by the flowing gas.

In most reactor designs, the catalyst is propelled upwardly through a riser reactor zone where the catalyst contacts a feed. The coked or deactivated catalyst
10 particles are disengaged from the products and any un-reacted feed. After stripping, the catalyst particles are transferred to a regenerator for regeneration. The regenerated catalyst then flows downwardly from the regenerator to the bottom of the riser reactor, and the cycle is repeated.

The cycles of reaction and regeneration are carried out at high temperatures
15 and high flow rates. Collisions and abrasions between catalyst particles themselves, between the particles and reactor walls and between the particles and other parts of the unit tend to cause physical breakdown of the original particles into smaller particles known as fines. This physical breakdown is called attrition. The fines usually have particle diameters smaller than about 20 microns -- much smaller than the starting
20 particles. Most commercial reactors are fitted with cyclones to recover the fines, and/or with electrostatic precipitators to prevent the fines from becoming airborne.

Catalysts with higher attrition resistance are desirable because, among other reasons, fewer fines are generated for disposal, less environmental impact is caused by un-recoverable airborne particulates, operating costs are lower, and less catalyst is
25 required due to reduced catalyst consumption.

Summary of the Invention

The present invention provides a method for making a catalyst comprising forming a mixture comprising an alumina sol, and silicoaluminophosphate molecular sieves comprising pores having a diameter in the range of from about 3 Angstroms to
5 about 5 Angstroms, and drying said mixture.

Detailed Description of the Invention

Hydrocarbon and oxygenate conversion catalysts, such as fluid catalytic cracking (FCC) catalysts and methanol-to-olefins (MTO) catalysts, respectively, are used most frequently in fluidized bed or moving bed systems. As a result, such
10 catalysts constantly are exposed to harsh chemical and physical conditions both during the hydrocarbon and oxygenate conversion reactions, and during catalyst regeneration.

The present invention relates to methods for making such catalysts to increase their attrition resistance. The method involves mixing molecular sieves with an
15 alumina sol and then drying the mixture.

Hydrocarbon conversion catalysts and oxygenate conversion catalysts generally have several components in their formulation: a microporous zeolitic or microporous non-zeolitic molecular sieve, an inorganic oxide matrix, and optionally other materials and modifiers, such as a clay.

20 Suitable molecular sieves include small pore, non-zeolitic microporous crystalline frameworks. The crystalline frameworks are three-dimensional and have well defined pore diameters. Small pore molecular sieves are defined herein as molecular sieves with pores having a diameter in the range of from about 3.0 Angstroms to about 5.0 Angstroms.

25 Suitable non-zeolitic molecular sieves include, but are not necessarily limited to silicoaluminophosphates ("SAPO's"). SAPO's have a three-dimensional

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microporous crystalline framework of PO_2^+ , AlO_2^- , and SiO_2 tetrahedral units. Suitable SAPO's include, but are not necessarily limited to SAPO-17, SAPO-18, SAPO-34, SAPO-44, and mixtures thereof. A preferred SAPO is SAPO-34, which may be synthesized according to US-A-4,440,871, incorporated herein by reference, and *Zeolites*, Vol. 17, pp 512-522 (1996), incorporated herein by reference.

SAPO's with substituents also may be used in the present invention. Suitable substituted SAPO molecular sieves include, but are not necessarily limited to "MeAPSO's" and "MeAPO's." MeAPSO's contain at least some silicon in their framework. MeAPO's may or may not contain silicon. Examples of suitable metals (Me) are nickel, iron, cobalt, manganese and magnesium.

SAPO, MeAPO and MeAPSO molecular sieves can be modified further by using, for example, magnesium, calcium, strontium, barium, lanthanides, actinides and mixtures thereof. A preferred modifier is strontium. Preferred modified SAPO's are strontium modified SAPO-17 (Sr-SAPO-17), strontium modified SAPO-18 (Sr-SAPO-18) and strontium modified SAPO-34 (Sr-SAPO-34).

The amount of the molecular sieve used in the mixture should form a catalyst composition having in the range of from about 3 wt% to about 99 wt%, preferably from about 5 wt% to about 90 wt%, and most preferably from about 10 wt% to about 80 wt% molecular sieve.

To make molecular sieves useful as catalysts in fluidized bed or moving bed reactor systems, an inorganic oxide matrix usually is needed in the catalyst formulation to provide physical strength and better heat transfer, among other desirable properties. A preferred inorganic oxide matrix is formed from a sol comprising an alumina sol. The term "alumina sol" means that the sol predominantly comprises alumina. Even an alumina sol may contain small amounts of silicon atoms.

The inorganic oxide sol in the catalyst essentially is a "glue" which binds the group of catalyst components together. A preferred sol has a relatively low viscosity.

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Upon drying the inorganic oxide sol, an inorganic oxide matrix is formed. Preferably, the individual catalyst components which are "glued" together by the matrix are in the range of about 0.3 to about 10.0 microns in size. The inorganic oxide matrix formed between the individual catalyst components in the final product has a measurable
5 diameter of less than 100 microns.

An alumina sol useful in the present invention typically is derived from a material selected from the group consisting of aluminum chlorohydrate, peptized boehmite, and mixtures thereof. Aluminum chlorohydrate has a general formula of $\text{Al}_{13}\text{O}_4(\text{OH})_{24}\text{Cl}_7 \cdot 12\text{H}_2\text{O}$.

10 A preferred alumina sol is made by forming a solution of a starting material wherein the particle components do not form a gel. The pH of the alumina sol preferably is in the range of from about 2 to about 10. More preferably, the pH is in the range of from about 3 to about 9. The pH of the inorganic oxide sol can be measured using standard glass electrodes or other methods known to those of ordinary
15 skill in the art. The inorganic oxide sol may be made using a batch, continuous, or semi-continuous process.

A sufficient amount of the alumina sol is used to prepare the catalyst to cause the amount of the resultant aluminum oxide matrix in the finished catalyst to be in the range of from about 2 wt% to about 98 wt%, preferably from about 5 wt% to about 90
20 wt%, and more preferably from about 10 wt% to about 80 wt%.

In addition, separate alumina phases may be incorporated into the aluminum oxide matrix of the present invention. Materials that can be used to form such phases include, but are not necessarily limited to aluminum oxyhydroxide, γ -alumina, boehmite, diaspore, and transitional aluminas such as α -alumina, β -alumina, γ -
25 alumina, δ -alumina, ϵ -alumina, κ -alumina, and ρ -alumina. Aluminum trihydroxide, such as gibbsite, bayerite, nordstrandite, doyleite, and mixtures thereof, also can be used.

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Catalysts made according to the present invention also may contain other components, preferably a clay. Kaolin is a preferred clay. Preferably kaolin is used in an amount sufficient to form a finished catalyst composition comprising kaolin in the range of from about 10 wt% to about 90 wt%, preferably from about 15 wt% to about 85 wt%, and more preferably from about 20 wt% to about 80 wt%.

The molecular sieve, an alumina sol, and optionally a clay are mixed to form a slurry. The catalyst can be made using a batch, continuous, or semi-continuous mode. The mixing can be carried out at a temperature in the range of from about -10°C to about 50°C. Pressure and atmosphere are not critical. In a preferred embodiment, the mixing can be carried out at a pressure in the range of from about 100 kPa to about 500 kPa, and in an atmosphere of air or nitrogen. The resultant slurry may be colloid-milled in the range of from about one to about five times for a total time period in the range of from about 3 seconds to about 5 minutes to obtain a desired particle texture, particle size, and/or particle size distribution.

The slurry then is dried using known means. Preferably, the slurry is spray dried. In spray drying, the slurry is fed into a nozzle which breaks the slurry into small particles. The particles then are dried in a co-current or counter-current flow of air through the spray drier. A dry powder catalyst is recovered. Alternately, the dry powder catalyst may be ground in the range of from about one to about five times, for a total period of time in the range of from about one to about five hours, in order to obtain a desired particle size and/or particle size distribution.

The spray-dried catalysts, with or without further grinding, may be used without further treatment. In another embodiment, The spray-dried catalysts are calcined at an elevated temperature in the range of from about 400°C to about 1000°C, preferably in the range from about 500°C to about 850°C. The calcination time depends on the catalyst formulation and the temperature of calcination. The time should be in the range of from about 0.5 hours to about 48 hours, preferably from about 2 hours to about 24 hours. The pressure and the atmosphere used during

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calcination are not critical, and should be selected to give the desired oxidation states of any easily reducible or oxidizable elements present in the catalyst.

The sprayed dried catalysts also may be ion exchanged before or after the calcination. When aluminum chlorohydrate is used as the starting material, it is preferred to carry out the ion-exchange step, if performed, after calcination.

Catalysts made according to the present invention have increased attrition resistance properties. Resistance to attrition is a measurement of the hardness of a catalyst, or how well the catalyst resists wear under test or process conditions. A catalyst with good attrition resistance will last longer and is more desirable than a catalyst with poor attrition resistance. Poor attrition resistance leads to the production of more fines that may escape from the processing units and cause environmental problems.

The test used to measure attrition resistance according to the present invention is the "extended attrition test." A Jet Cup Attritor is used. A sample of 6 grams of the catalyst are tested for 4 hours. Attrition products (<20 microns) are measured gravimetrically and the data are used to calculate the attrition rate of the catalyst. An extended attrition index is obtained by measuring the amount by weight of particles smaller than about 2.6 microns generated during the test. Generally, the fewer particles having a diameter smaller than about 2.6 Angstroms produced, the more attrition resistant the catalyst. The attrition products also are analyzed for particle size distribution using a Leeds & Northrop Microtrac® Small Particle Analyzer. Surface areas and pore volumes are measured using Coulter Omnisorb® 610 instrument.

Catalysts made according to the present invention can be used for a number of purposes, preferably to convert oxygenates and/or hydrocarbons to lower molecular weight products, most preferably to lower olefins (ethylene, propylene, and butenes and mixtures thereof). Suitable reactors include, but are not necessarily limited to fixed bed reactors, moving bed reactors, fluidized bed reactors, or other similar types of reactors.

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Oxygenates can be converted to olefins by contacting a feed with a catalyst of the present invention under conditions effective to produce olefins. Preferred olefins are lower olefins -- ethylene, propylene, butenes, and mixtures thereof.

Oxygenates suitable for such conversions include, but are not necessarily
5 limited to aliphatic alcohols, aliphatic ethers, aliphatic carbonyl compounds (aldehydes, ketones, carboxylic acids, esters, carbonates and the like), alkyl halides, alkyl amines, and mixtures thereof. Preferred oxygenates are methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, dimethyl ether, methylethyl ether, diethyl ether, dimethyl carbonate, and mixtures thereof.

10 Effective conditions for oxygenate conversions are: temperature in the range of from about 200 °C to about 800°C; pressure in the range of from about 1 kPa to about 2 Mpa; Weight Hourly Space Velocity (WHSV) in the range of from about 0.01 h⁻¹ to about 10,000 h⁻¹. Because the feed may contain diluents and the catalyst may contain filler and/or binder materials, WHSV is calculated on the weight of the
15 oxygenate feed itself and the weight of the molecular sieve component in the catalyst.

The oxygenate feed may comprise an amount of diluent in the range of from about 0 wt% to about 95 wt% of the total feed. Suitable diluents include but are not necessarily limited to water (steam), CO₂, hydrogen, nitrogen, argon, and mixtures thereof.

20 After conversion, the products and any unreacted feedstock are separated from the catalyst, and the products are purified. Unreacted feedstock may be recycled back to the conversion reactor or otherwise disposed. Deactivated catalysts may be regenerated. Regeneration can be carried out in the conversion reactor or in a separate regeneration reactor. Regeneration usually is carried out at elevated temperatures, 350
25 °C to 950°C, and in the presence of an oxygen containing atmosphere. Treating a deactivated catalyst with hydrogen at elevated temperatures also may be effective to regenerate the catalytic performance of the oxygenate conversion catalyst.

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The catalysts also can be used to convert hydrocarbons to products having lower molecular weights than the feedstock hydrocarbons. Hydrocarbon feedstocks include, but are not necessarily limited to naphtha and similar hydrocarbons. The feedstocks comprise mostly non-aromatic compounds with at least five carbon atoms.

5 Preferred products comprise lower olefins (ethylene, propylene, and butenes) and aromatics.

Typical reaction conditions for hydrocarbon conversions are: temperature in the range of from about 250 °C to about 900°C; pressure in the range of from about 1 kPa to about 2 Mpa; WHSV in the range of from about 0.01 h⁻¹ to about 10,000 h⁻¹.

10 Because the feed may contain diluents and the catalyst may contain filler and/or binder materials, WHSV is calculated on the weight of the hydrocarbon feed itself and the weight of the molecular sieve component in the catalyst. Diluents such as water (steam), CO₂, hydrogen, nitrogen, and others can be mixed with the feedstock. The amount of diluent preferably comprises in the range of from about 0 wt% to about 95

15 wt% of the total feed.

The hydrocarbon feed is contacted with the catalyst in a conversion reactor under effective conditions for conversion. Suitable conversion reactors are fixed bed reactors, a moving bed reactors, fluidized bed reactors, or other similar types of reactors.

20 After conversion the products and any unreacted feedstock are separated from the catalyst, and the products are purified. Unreacted feedstock may be recycled back to the conversion reactor or otherwise disposed. Deactivated catalysts may be regenerated as previously described. Regeneration can be carried out in the conversion reactor or in a separate regeneration reactor.

25 The present invention will be better understood with reference to the following examples, which are intended to illustrate, but not to limit the scope or spirit of the invention. The invention is solely defined by the claims.

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EXAMPLE I

A catalyst was prepared as follows:

1.06 lb of Reheis® Chlorohydrol® (47wt% Al_2O_3) was dissolved in 4 lb of distilled water. To this solution was added 3.25 lb of Hydrite UF kaolin (from Dry Branch) and 1.29 lb of SAPO-34 (0.966 solids), obtained from UOP. The resultant mixture was colloid milled twice and was washed from the colloid mill with an additional 1 lb of distilled water. The pH of the colloid-milled product, a slurry, was 4.0. The slurry was spray dried in an Anhydro PV Spray Drier® at Moyno pump setting 2.1; 10,000 rpm; 288°C inlet temperature and the outlet temperature between 177°C and 160°C. 2.2 lb of coarse catalyst product and 0.9 lb of fines were collected from the spray drier. The spray dried powder was calcined at 816°C for 2 hours.

The resulting catalyst was subjected to the extended attrition test to determine its extended attrition index. The results of this experiment and the following experiments are shown in TABLE I. The test catalyst exhibited a good extended attrition index of 11. Commercially available catalysts also were tested under similar attrition testing conditions. The series of commercial catalysts tested were Engelhard Reduction®, Grace Spectra®, Grace Ramcat®, Akzo Advance®, and Akzo Vision® catalysts. The catalyst prepared according to this example was significantly more attrition resistant than the tested commercial catalysts.

EXAMPLE II

A catalyst was prepared as described in EXAMPLE I, except that after spray drying, the spray-dried powder was calcined at 760°C for two hours.

The resultant catalyst was subjected to the extended attrition test to determine its extended attrition index. As shown in TABLE I, the catalyst exhibited a good extended attrition index of 10. The test catalyst was significantly more attrition resistant than the tested commercial catalysts.

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Furthermore, the catalyst calcined at the lower temperature as prepared in this EXAMPLE was more attrition resistant.

EXAMPLE III

Another catalyst was prepared as follows:

5 1.06 lb of Reheis® Chlorohydrol® (47wt% Al_2O_3) was dissolved in 4 lb of distilled water. To this solution was added 2.00 lb of Hydrite® UF kaolin, 2.58 lb of SAPO-34 (0.966 solids), obtained from UOP and an additional 1.0 lb of water to form a slurry. The resultant mixture was colloid milled twice and was washed from the colloid mill with an additional 1.1 lb of distilled water. The pH of the colloid-milled
10 product, a slurry, was 3.7. The slurry was spray dried in an Anhydro PV Spray Drier at Moyno pump setting 2.1; 10,000 rpm; 288°C inlet temperature and the outlet temperature between 177°C and 160°C. 2.2 lb of coarse catalyst product and 0.9 lb of fines were collected from the spray drier. The spray dried powder was calcined at 816°C for 2 hours.

15 The resulting catalyst was subjected to the extended attrition test to determine its extended attrition index. As shown in TABLE I, the catalyst exhibited a good extended attrition index of 7. The test catalyst was significantly more attrition resistant than the tested commercial catalysts.

EXAMPLE IV

20 A catalyst of the present invention was prepared similar to EXAMPLE I, except that after spray drying, the spray-dried powder was calcined at 760°C for two hours.

 The resultant catalyst was subjected to the extended attrition test to determine its extended attrition index. As shown in TABLE I, the calcined catalyst exhibited a
25 good extended attrition index of 6. The test catalyst was significantly more attrition resistant than the tested commercial catalysts.

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Furthermore, the catalyst calcined at the lower temperature as prepared in this EXAMPLE was more attrition resistant.

TABLE I

Sample	Surface Area (m ² /g) Pore Volume (cc/g)	Extended Attrition	% Microfines	Extended Attrition Index
Example I	208/0.41	47	23	11
Example II	210/0.18	51	20	10
Example III	357/0.21	39	18	7
Example IV	378/0.22	42	15	6

5 Attrition test results showed that catalysts of the present invention made significantly fewer microfines than commercial catalysts. Depending on the formulation and preparation conditions, the catalysts of the present invention produced microfines in a range of from about 15 to about 23. Under comparable conditions, commercial catalysts generated microfines in the range of from about 18
10 to about 52. Furthermore, the catalysts calcined at a lower temperature (760°C) were more attrition resistant than the catalysts calcined at a higher temperature (816°C).

Molecular sieves themselves generally are not considered to be good binding materials. Normally, the amount of fines produced by a catalyst increases with the molecular sieve content. It was surprising to observe that the test catalysts containing
15 the highest amounts of SAPO-34 (Ex. III and Ex. IV, about 50 wt%) produced fewer microfines than the catalysts containing less SAPO-34 (Ex I and Ex. II, about 25 wt%).

The foregoing results demonstrate that catalysts prepared according to the method of this invention produced fewer microfines and showed increased attrition
20 resistance compared to commercially available catalysts.

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Persons of ordinary skill in the art will recognize that many modifications may be made to the present invention without departing from the spirit and scope of the present invention. The embodiment described herein is meant to be illustrative only and should not be taken as limiting the invention, which is defined in the following

5 claims.

What is claimed is:

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- 1 1. A method for making a catalyst comprising:
2 forming a mixture comprising an alumina sol and a silicoaluminophosphate
3 molecular sieve having pores of a diameter less than about 5 Angstroms; and
4 drying said mixture to form a catalyst.
- 1 2. The method of claim 1 wherein said drying includes spray drying at a first
2 elevated temperature to form a spray dried catalyst.
- 1 3. The method of any one of the preceding claims further including calcining
2 said spray dried catalyst at a second elevated temperature to form a calcined catalyst.
- 1 4. The method of any one of the preceding claims wherein said
2 silicoaluminophosphate molecular sieves is selected from the group consisting of
3 SAPO-17, SAPO-18, SAPO-34, SAPO-44, and mixtures thereof.
- 1 5. The method of any one of the preceding claims wherein said alumina sol is a
2 compound selected from the group consisting of aluminum chlorohydrate and peptized
3 boehmite.
- 1 6. The method of any one of the preceding claims wherein said alumina sol has
2 a pH in the range of from about 2 to about 10.
- 1 7. The method of any one of the preceding claims wherein said catalyst
2 comprises of an amount of aluminum oxide produced from said alumina sol in the
3 range of from about 2 wt% to about 98 wt% of said catalyst.
- 1 8. The method of any one of the preceding claims wherein said catalyst
2 comprises an amount of said molecular sieves, comprising in the range of from about
3 3 wt% to about 99 wt%.
- 1 9. The method of claim 3 wherein said second elevated temperature is in the
2 range of from about 400°C to 1000°C.

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1 10. A catalyst comprising:
2 a silicoaluminophosphate molecular sieve having pores of a diameter less than
3 about 5 Angstroms; and
4 an aluminum oxide matrix derived from an alumina sol.

1 11. The catalyst of claim 10 further including clay.

1 12. The catalyst of claim 10 wherein:
2 said molecular sieve comprises from about 3 wt% to about 99 wt% of said
3 catalyst; and
4 said aluminum oxide matrix comprises from about 2 wt% to about 98 wt% of said
5 catalyst.

1 13. The catalyst of claim 11 wherein said catalyst further includes from about 10
2 wt% to about 90 wt% of said clay.

1 14. The catalyst of claim 10 wherein said silicoaluminophosphate molecular
2 sieve is selected from the group consisting of SAPO-17, SAPO-18, SAPO-34, SAPO-
3 44 and mixtures thereof.

INTERNATIONAL SEARCH REPORT

Int l Application No
PCT/US 98/21836

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J29/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 973 792 A (LEWIS JEFFREY M O ET AL) 27 November 1990 see example 1	1-14
Y	US 5 248 647 A (BARGER PAUL T) 28 September 1993 see example 2	1-14
Y	US 5 173 463 A (MACEDO JOSE C D) 22 December 1992 see column 3, line 33 - column 3, line 36 see column 4, line 59 - column 5, line 22	1-14
Y	GB 1 315 553 A (GRACE W R & CO) 2 May 1973 see page 1, line 56 - page 1, line 76 see page 2, line 27 - page 2, line 82	1-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schwaller, J-M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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